

J1036 U.S. PRO
09/843519
04/27/01

RPR 7048

TRANSLATION

96-11-71

(19) Japan Patent Office (JP)

(11) Patent Application Kokai
No.: H8-169713

(12) Patent Official Gazette (A)

(51) Int. Cl⁶

I.D. No. Interbureau Classification No. F1.

(43) Kokai (Public Disclosure) date:
7/2/1996

C 01 F	17/00	B	9439-4G
C 04 B	35/50		
C 25 B	9/00	304	
H 01 M	8/02	K	9444-4K
	8/12		9444-4K

Number of claims: 3 (6 pages)

21. Application No. H6-311722

22. Application No. 12/15/1994

71. Applicant: 000176660

Santoku Kinzoku Kogyo K.K.

14-34, 4 chome, Fukae Kitamachi, Higashinada-ku, Kobe-shi, Hyogo-ken

72. Inventor: Naoki Fujii

Santoku Kinzoku Kogyo K.K.

14-34, 4 chome, Fukae Kitamachi, Higashinada-ku, Kobe-shi, Hyogo-ken

74. Agent: Patent attorney, Hajime Sakai (and one other)

54. [Title of the Invention]

Cerium Type Sinterable Composite Oxide, the Cerium Type Composite Oxide

Sintered Body and the Method to Produce These.

57. [Summary]

[Structure]

The cerium containing type sinterable composite oxide of which the relative density of the sintered body, when it was sintered at 1250 to 1600 °C, is 95 % or higher, in the cerium type composite oxide which includes 50 to 99.9 mole % of cerium oxide, and the sintered body that was sintered at 1250 to 1600 °C, and the method to produce the above mentioned sintered body in which the composite salt precipitate is obtained

from the various raw material metal ion - containing solution, in which the metal oxide equivalent concentration is adjusted to 30 to 500 g / L, and this composite salt precipitate is baked at 700 to 1200 °C, and thereafter, it is sintered at 1250 to 1600 °C.

[Effect]

The above mentioned composite oxide has excellent sintering ability at low temperature, and excellent processing ability, and it is useful as the raw material for the electrolyte member of the solid electrolytes. The above mentioned sintered body is low cost, and its processing is easy, and the sintered density is high, and when it is used as the electrolyte, the diffusion of gas can be restricted, and it has excellent electrical characteristics. The above mentioned production method can produce the above mentioned sintered body easily with good reproducibility.

[Scope of the Patent Application]

[Claim 1]

The cerium containing type sinterable composite oxide which is characterized by the fact that the relative density of the sintered body, when it was sintered at 1250 to 1600 °C, is 95 % or higher, in the cerium type composite oxide which includes 50 to 99.9 mole % of cerium oxide, (*the following part of this sentence, which occurs in several places in this patent, is very poorly written, but from reading the examples and the rest of the text, it most likely means the following, Translator*) and also 0.1 to 50 mole % of one or more of the oxides of the alkaline earth metals such as magnesium oxide, calcium oxide, strontium oxide, barium oxide and / or transition metal oxides other than cerium, such as zirconium oxide, hafnium oxide, niobium oxide, tantalum oxide, etc. or mixtures of these.

U

[Claim 2]

The cerium type composite oxide sintered body in which the relative density is 95 % or

higher, and where the cerium type composite oxide which includes 50 to 99.9 mole % of cerium oxide, and also 0.1 to 50 mole % of one or more of the oxides of the alkaline earth metals such as magnesium oxide, calcium oxide, strontium oxide, barium oxide and / or transition metal oxides other than cerium, such as zirconium oxide, hafnium oxide, niobium oxide, tantalum oxide, etc. or mixtures of these, is sintered at 1250 to 1600 °C.

[Claim 3]

The method to produce the above mentioned cerium type composite oxide sintered body characterized by the fact that, the solution which contains 50 to 99.9 mole % of cerium ions, and 0.1 to 50 mole % of one or more alkaline earth metal ions or transition metal ions, excluding cerium, such as magnesium ions, calcium ions, strontium ions, barium ions, zirconium ions, hafnium ions, niobium ions, tantalum ions, or a mixture of these, is prepared, and the concentration of the said solution is adjusted to be 30 to 500 g / L of the metal (converted to the oxide basis) that was included, and thereafter, it is mixed with an aqueous ammonium solution, an aqueous ammonium carbonate solution, an aqueous ammonium bicarbonate solution, an aqueous oxalic acid solution or a mixture of these, and the composite salt precipitate is obtained, and the obtained composite salt precipitate is baked at 700 to 1200 °C, and thereafter, it is sintered at 1250 to 1600 °C.

[Detailed Explanation of the Invention]

[0001]

[Field of Utilization in Industry]

This invention relates to the cerium type sinterable composite oxide, which has excellent sintering ability at low temperature, and which can be used as the raw material for the electrolyte member of the solid electrolyte fuel cell (SOFC) and the high temperature steam electrolysis device, etc., and the sintered body where the said oxide

was sintered, and the method to produce these.

[0002]

[Existing Technique]

Until now, the cerium type composite oxide was made by the method in which the powdered cerium oxide was used as the main component, and the powdered oxides of other components, and the carbonate salts and / or hydroxides, etc., are crushed, and mixed, and thereafter, it is sintered. Such composite oxide has been used as the raw material for the electrolyte member of the SOFC and the high temperature steam electrolysis device, etc., and these are required to be of high density after sintering, and also to have the physical properties that can restrict the gas diffusion to the highest degree possible.

[0003]

However, the cerium type composite oxide that was produced by the existing production method, has poor sintering ability at low temperature, and it can not attain a relative density of 95 % or higher, unless it is sintered at 1650 °C or higher. When the sintering was done at such a high temperature, the sintered body that is obtained, has poor processing ability, and it is difficult to restrict the gas diffusion, and also the cost becomes high, and these are the problems.

[0004]

In addition, in the case when the formed body is produced by sintering the existing cerium type composite oxides, water, etc., must be added as the forming assist agent, and the production process becomes a nuisance, and sometimes the physical properties of the sintered body that is obtained, are impaired by the addition of these additives.

[0005]

[Problem That this Invention Intends to Solve]

Therefore, the objective of this invention is to offer the cerium type sinterable composite oxide which has excellent sintering ability at low temperature, and excellent processing ability and good forming ability. Another objective of this invention is to offer the cerium type composite oxide sintered body with which the processing is easy, the gas diffusion can be restricted, and also of which the cost is low. Another objective of this invention is to offer the method to produce the cerium type composite oxide sintered body by which the above mentioned sintered body can be prepared with good reproducibility, and easily, and at low cost, and also that is effective in industry.

[0006]

[Method to Solve the Problem]

In this invention, the cerium type containing sinterable composite oxide (from now on, it will be called composite oxide A) which is characterized by the fact that the relative density of the sintered body, when it was sintered at 1250 to 1600 °C, is 95 % or higher, can be obtained from the cerium type composite oxide which includes 50 to 99.9 mole % of cerium oxide, and also 0.1 to 50 mole % of one or more of the oxides of the alkaline earth metals such as magnesium oxide, calcium oxide, strontium oxide, barium oxide and / or transition metal oxides other than cerium, such as zirconium oxide, hafnium oxide, niobium oxide, tantalum oxide, etc. or mixtures of these. Further, by this invention, the method to produce the above mentioned cerium type composite oxide sintered body characterized by the fact that the solution which contains 50 to 99.9 mole % of cerium ions, and 0.1 to 50 mole % of one or more alkaline earth metal ions or transition metal ions, excluding cerium, such as magnesium ions, calcium ions, strontium ions, barium ions, zirconium ions, hafnium ions, niobium ions, tantalum ions, or a mixture of these, is prepared, and the concentration of the said solution is adjusted to be 30 to 500 g / L of the metal (converted to the oxide basis) that was included, and

thereafter, it is mixed with an aqueous ammonium solution, an aqueous ammonium carbonate solution, an aqueous ammonium bicarbonate solution, an aqueous oxalic acid solution or a mixture of these, and the composite salt precipitate is obtained, and the obtained composite salt precipitate is baked at 700 to 1200 °C, and thereafter, it is sintered at 1250 to 1600 °C.

[0007]

Next, this invention will be explained in detail. The composite oxide A of this invention includes cerium oxide as its main component, and it includes specific metal oxides which will be explained later, and when it is sintered at 1250 to 1600 °C, the relative density of the sintered body is 95 % or higher. In this case, the relative density of the sintered body means the value calculated by,

$$\text{Relative density (\%)} = (\text{apparent density} / \text{theoretical density}) \times 100$$

Here, the theoretical density is where the lattice constants of the composite oxide before sintering are obtained, using sodium chloride as an internal standard on the (200) plane diffraction basis, and the diffraction angle of the sample (sintered body of composite oxide) was compensated for, and the theoretical density was calculated from that value. The apparent density is the value that was obtained from the mass and the volume of the sample.

[0008]

The composite oxide A of this invention includes 50 - 99.9 mole % of cerium oxide. When the cerium oxide content is less than 50 mole %, the sintering ability is poor, and when it is sintered at 1250 °C or higher, the relative density of the sintered body does not become 95 % or higher.

[0009]

The composite oxide A of this invention includes 0.1 to 50 mole % of one or more of the oxides of the alkaline earth metals such as magnesium oxide, calcium oxide, strontium oxide, barium oxide and / or transition metal oxides other than cerium, such as zirconium oxide, hafnium oxide, niobium oxide, tantalum oxide, etc. or mixtures of these. Yttrium oxide, lanthanum oxide, praseodymium oxide, neodymium oxide, samarium oxide, gadolinium oxide, etc., can also be listed as the above mentioned oxides. These components are already known as the effective components of the cerium type composite oxide. In addition to these metal oxides, if the relative density after sintering is 95 % or higher, some other components, for example, the ones which are inevitably mixed in during the production due to the raw materials, etc., are permissible too.

[0010]

The form of the composite oxide A of this invention should be preferably granular or powder, and it should be in the range where the average grain diameter is 0.1 to 3 μm , the specific surface area is 5 to 20 m^2/g , and the tap density is 1.0 to 1.6 g/cm^3 .

[0011]

Concerning the production method of the above mentioned composite oxide A, first, the solution which contains 50 to 99.9 mole % of cerium ions, and 0.1 to 50 mole % of one or more alkaline earth metal ions or transition metal ions, excluding cerium, such as magnesium ions, calcium ions, strontium ions, barium ions, zirconium ions, hafnium ions, niobium ions, tantalum ions, or a mixture of these, is prepared. Yttrium ions, lanthanum ions, praseodymium ions, neodymium ions, samarium ions, gadolinium ions, etc., can be listed as the transition metal ions other than the above mentioned cerium. In order to obtain the solution that includes these ions, each ion can be mixed as an aqueous solution of nitric acid, and thus it can be obtained.

[0012]

Next, the concentration of the obtained solution is adjusted to 30 to 500 g / L on an included metal oxide equivalent basis, preferably it should be adjusted to 300 to 500 g / L. If the metal oxide equivalent concentration of this solution exceeds 500 g / L, it causes crystallization, and it does not become a uniform solution, and if the concentration is less than 30 g / L, the crystals of the precipitate grow, and it gives ill effects to the subsequent reaction process.

[0013]

Thereafter, the concentration adjusted solution is mixed with an aqueous ammonium solution, an aqueous ammonium carbonate solution, an aqueous ammonium bicarbonate solution, an aqueous oxalic acid solution or a mixture of these, and the composite salt precipitate is obtained. At this time, the concentrations of these solutions are, in the case of the ammonium water, preferably 1 to 2 N, more preferably 1 to 1.5 N, and in the case of an aqueous solution of ammonium carbonate or ammonium bicarbonate, it should be 50 to 200 g / L, preferably 100 to 150 g / L, and in the case of oxalic acid, it should be 50 to 100 g / L, preferably 50 to 60 g / L. Also, the mixing ratio of the above mentioned concentration adjusted solution and the aqueous ammonium solution, the aqueous ammonium carbonate solution, the aqueous ammonium bicarbonate solution, the aqueous oxalic acid solution or the mixture of these, should be 1 : 1 to 1 : 10 as the weight ratio. For example, the composite hydroxide, the composite carbonate salt, etc., can be listed as the composite precipitate that can be obtained at this time.

[0014]

Next, the obtained composite salt precipitate is preferably dried, and thereafter, it is baked at 700 to 1200 °C, preferably at 750 to 1000 °C, for 1 to 10 hours, and thus, the desired composite oxide A with excellent sintering ability at low temperature, can be

obtained. At this time, if the temperature is outside the range of 700 to 1200 °C, the composite oxide A with desired relative density, can not be obtained.

[0015]

The cerium type composite oxide sintered body of this invention, is the sintered body where the above mentioned composite oxide A is sintered at 1250 to 1600 °C, and of which the relative density is 95 % or higher.

[0016]

In the production method of the above mentioned sintered body of this invention, after the composite oxide A is prepared, it is sintered at 1250 to 1600 °C, preferably for 1 to 20 hours. Preferably, the obtained composite oxide A is crushed into an average grain diameter of 0.1 to 3 μm by an automatic mortar and pestle, etc., and it is formed into the desired shape using an already known forming machine, etc., and thereafter, it is sintered in an electric furnace, etc. At this time in the forming process, it can be formed easily without using a forming assist agent such as water, which used to be necessary in the existing cerium type composite oxide. Also, the crushing process before forming can be done more easily compared with in the existing method.

[0017]

[Effect of the Invention]

When it is sintered at 1250 to 1600 °C, the composite oxide A of this invention will have a relative density of 95 % or higher, and it has excellent sintering ability at low temperature and excellent processing ability, therefore, it is useful as the raw material for the electrolyte member of the solid electrolyte. Also, the sintered body of this invention is made out of the above mentioned composite oxide A, therefore, the processing is easier, compared with the sintered body of the existing cerium type composite oxide, and the sintered density is high, therefore, when it is used as the

electrolyte, the diffusion of gas is restricted, and it has excellent electrical characteristics, and it is low cost. In addition, the production method of this invention has good reproducibility, and it is low cost and easy, therefore, it is effective in industry.

[0018]

[Actual Examples]

Next, this invention will be explained more in detail, referring to Examples and Comparisons, but this invention is not limited to these.

[0019]

[Example 1]

An aqueous solution of cerium nitrate (a product of Santoku Kinzoku K.K.: this contains 500 g / L as cerium oxide) and an aqueous solution of samarium nitrate (a product of Santoku Kinzoku K.K.: this contains 250 g / L as samarium oxide) were mixed in the way that it becomes, $\text{CeO}_2 : \text{SmO}_{1.5} = 80 : 20$ (mole ratio) when converted to the oxides, and the solution with a total weight of 500 g was prepared. Here, $\text{SmO}_{1.5}$ has the same meaning as in the below listed Chemical Formula 1.

[0020]

[Chemical Formula 1]

$\text{SmO}_{1.5}$

[0021]

Next, 3 L of an aqueous solution of ammonium carbonate, which was separately prepared to have a concentration of 160 g / L, was added into the obtained solution, and it was reacted, and the composite salt precipitate was obtained. The precipitate that was obtained, was not matured, and it was quickly filtered, and it was dried at 150

°C for 20 hours, and thereafter, it was baked at 900 °C for 3 hours. The obtained baked material was crushed by an automatic mortar and pestle, and the composite oxide, of which the average grain diameter was 37 µm, was obtained. It took 15 minutes to crush it.

[0022]

2.5 g of the obtained composite oxide was formed using a rectangular tablet forming machine, (2.5 cm x 0.5 cm, made by Toyo Yuatsu Kikai K.K.) and the press (made by Shimazu Seisakusho K.K.). Next, the composite oxide with the same composition, was spread as a bed of sand on an alumina board (commercial name "SSA - A alumina" purity level of 99.5 %, a product of Nihon Kagaku Togyosha K.K.), and the above mentioned composite oxide tablet that was formed, was placed on the sand bed, and the temperature was raised to the sintering temperature indicated in Table 1, with a temperature increase rate of 10 °C / minute, using an electric furnace, and it was sintered at that temperature in air for 10 hours. Thereafter, the temperature was cooled to room temperature at a temperature decrease rate of 10 °C / minute, and the sintered body was obtained. The obtained sintered body was polished, gradually, in order, using water resistant polishing papers (#80, #180, #320, #600, #1000, #1500). Thereafter, the outer diameter of the polished sintered body was measured by a caliper, and the weight was measured by an electronic balance (accuracy of 0.1 mg), and the apparent density was measured. The apparent density and the relative density of the sintered bodies at each temperature are indicated in Table 1. Here, the theoretical density was obtained as follows: the obtained sintered body was crushed, and the powder X-ray diffraction pattern was obtained, and it was calculated from the lattice constants.

[0023]**[Example 2]**

An aqueous solution of cerium nitrate (a product of Santoku Kinzoku K.K.: this contains 500 g / L as cerium oxide) and an aqueous solution of samarium nitrate (a product of Santoku Kinzoku K.K.: this contains 250 g / L as samarium oxide), and a calcium nitrate solution [calcium carbonate (a product of Wako Junyaku Kogyo K.K.) was dissolved in nitric acid, and the concentration was adjusted to be 400 g / L, as calcium oxide] were mixed in the way that it became, $\text{CeO}_2 : \text{SmO}_{1.5} : \text{CaO} = 85 : 10 : 5$ (mole ratio) when converted to the oxides, and the solution with a total weight of 500 g was prepared. Thereafter, the composite oxide was obtained in the same way as in Example 1, and the sintered body was prepared in the same way as that in Example 1, except that the sintering temperature was changed to 1500 °C. The apparent density, the theoretical density, and the relative density were measured. The results are shown in Table 1.

[0024]**[Example 3]**

An aqueous solution of cerium nitrate (a product of Santoku Kinzoku K.K.: this contains 500 g / L as cerium oxide) and an aqueous solution of samarium nitrate (a product of Santoku Kinzoku K.K.: this contains 250 g / L as samarium oxide), and a strontium nitrate solution [strontium nitrate (a product of Wako Junyaku Kogyo K.K.) was dissolved in water, and the concentration was adjusted to be 400 g / L, as the strontium oxide] were mixed in the way that it becomes, $\text{CeO}_2 : \text{SmO}_{1.5} : \text{SrO} = 85 : 10 : 5$ (mole ratio) when converted to the oxides, and the solution with a total weight of 500 g was prepared. Thereafter, the composite oxide was obtained in the same way as in Example 1, and the sintered body was prepared in the same way as that in Example 1, except that the sintering temperature was changed to 1500 °C. The apparent density, the theoretical density, and the relative density were measured. The results are shown in Table 1.

[0025]**[Example 4]**

An aqueous solution of cerium nitrate (a product of Santoku Kinzoku K.K.: this contains 500 g / L as cerium oxide) and an aqueous solution of samarium nitrate (a product of Santoku Kinzoku K.K.: this contains 250 g / L as samarium oxide), and a barium nitrate solution [barium nitrate (a product of Wako Junyaku K.K.) was dissolved in water, and the concentration was adjusted to be 50 g / L, as the barium oxide] were mixed in the way that it becomes, $\text{CeO}_2 : \text{SmO}_{1.5} : \text{BaO} = 85 : 10 : 5$ (mole ratio) when converted to the oxides, and the solution with the total weight of 500 g was prepared. Thereafter, the composite oxide was obtained in the same way as in Example 1, and the sintered body was prepared in the same way as that in Example 1, except that the sintering temperature was changed to 1500 °C. The apparent density, the theoretical density, and the relative density were measured. The results are shown in Table 1.

[0026]**[Comparison 1]**

Granules of cerium oxide and samarium oxide were weighed by an electronic balance to make the $\text{CeO}_2 : \text{SmO}_{1.5} = 80 : 20$ (mole ratio) and the total weight became 50 g, and it was crush - mixed for 30 minutes by an automatic mortar and pestle (a product of Nitto Kagaku K.K.). Then, it was transferred into an alumina crucible, and the temperature was raised to 1350 °C by an electric furnace, at a temperature increase rate of 10 °C / minutes, and it was sintered in air for 10 hours. Thereafter, it was cooled to room temperature at a cooling rate of 10 °C / minutes. Then, it was crushed the same as in Example 1, and the composite oxide of which the average grain diameter was 1.79 μm, was obtained. It took twice as long a time (30 minutes) to crush this, as in the case of Example 1. About 20 mL of water was added into 1.9 g of the obtained composite oxide, as the forming assist agent, and it was mixed for 15 minutes in an agate mortar and pestle.

[0027]

This was formed using a rectangular tablet forming machine, (2.5 cm x 0.5 cm, made by Toyo Yuatsu Kikai K.K.) and a press (made by Shimazu Seisakusho K.K.). Next, the composite oxide of the same composition, was spread as a bed of sand on an alumina board (commercial name "SSA - A alumina" purity level of 99.5 %, a product of Nihon Kagaku Togyosha K.K.), and the above mentioned composite oxide tablet that was formed, was placed on the sand bed, and the temperature was raised to the sintering temperature indicated in Table 1, with a temperature increase rate of 10 °C / minute, using an electric furnace, and it was sintered at that temperature in air for 10 hours. Thereafter, the temperature was cooled to room temperature at a temperature decrease rate of 10 °C / minute, and the sintered body was obtained. By the way, in the case when the forming assist agent was not added, the sintering ability did not improve. The obtained sintered body was treated the same as that in Example 1, and thereafter, the apparent density, the theoretical density and the relative density were measured. The results are shown in Table 1.

[0028]**[Comparison 2]**

Granules of cerium oxide and samarium oxide and calcium carbonate were weighed by an electronic balance to make the $\text{CeO}_2 : \text{SmO}_{1.5} : \text{CaO} = 85 : 10 : 5$ (mole ratio) and the total weight became 50 g, and thereafter, the composite oxide was prepared in the same way as that in Comparison 1. It was treated the same as that in Comparison 1, except that the obtained composite oxide was sintered at 1650 °C, and the apparent density, the theoretical density and the relative density were measured. The results are shown in Table 1.

[0029]

[Comparison 3]

Granules of cerium oxide and samarium oxide and strontium carbonate were weighed by an electronic balance to make the CeO₂ : SmO_{1.5} : SrO = 85 : 10 : 5 (mole ratio) and the total weight became 50 g, and thereafter, the composite oxide was prepared the same way as that in Comparison 1. The obtained composite oxide was treated the same as that in Comparison 1, except that the obtained composite oxide was sintered at 1600°C, and the apparent density, the theoretical density and the relative density were measured. The results are shown in Table 1.

[0030]

[Comparison 4]

Granules of cerium oxide and samarium oxide and barium carbonate were weighed by an electronic balance to make the CeO₂ : SmO_{1.5} : BaO = 85 : 10 : 5 (mole ratio) and the total weight became 50 g, and thereafter, the composite oxide was prepared in the same way as that in Comparison 1. The obtained composite oxide was treated the same as that in Comparison 1, except that the obtained composite oxide was sintered at 1600°C, and the apparent density, the theoretical density and the relative density were measured. The results are shown in Table 1.

[0031]

[Table 1]

	CeO ₂ (mole)	SmO _{1.5} (mole)	MO (mole)	theoretical density (g / cm ³)	Sintering temp. (°C)	Apparent density (g / cm ³)	Relative density (%)
Example 1	0.80	0.20	—	7.133	1650	6.952	97.5
					1450	7.035	98.6
					1250	6.973	97.8
					1150	6.395	89.7
					1050	5.256	73.7
Example 2	0.85	0.10	0.05 (CaO)	6.961	1500	6.627	95.2
Example 3	0.85	0.10	0.05 (SrO)	6.982	1500	6.793	97.3
Example 4	0.85	0.10	0.05 (BaO)	7.132	1500	6.875	96.4
Com. 1	0.80	0.20	—	7.133	1650	6.721	94.2
					1500	6.211	87.1
					1450	6.047	84.8
					1350	5.164	72.4
Com. 2	0.85	0.10	0.05 (CaO)	6.961	1650	5.924	85.1
Com. 3	0.85	0.10	0.05 (SrO)	6.982	1600	6.088	87.2
Com. 4	0.85	0.10	0.05 (BaO)	7.132	1600	6.012	84.3

Com. means Comparison.

[The remainder of this page and the following half page are corrections, and these corrections were made before starting the translation, Translator]

96-11-71

(19)日本国特許庁 (JP)

(2) 公開特許公報 (A)

(11)特許出願公開番号

特開平8-169713

(43)公開日 平成8年(1996)7月2日

(51)Int.Cl.

C01F 17/00

C04B 35/50

C25B 9/00

H01M 8/02

8/12

識別記号 庁内整理番号

B 9439-4G

304

K 9444-4K

9444-4K

F I

技術表示箇所

審査請求 未請求 請求項の数 3 O.L (全 6 頁)

(21)出願番号

特願平8-311722

(22)出願日

平成6年(1994)12月15日

(71)出願人 000176660

三徳金属工業株式会社

兵庫県神戸市東灘区深江北町4丁目14番34号

(72)発明者 藤井 直樹

神戸市東灘区深江北町4丁目14番34号 三
徳金属工業株式会社内

(74)代理人 弁理士 潤井一 (外1名)

(54)【発明の名称】セリウム系焼結性複合酸化物、セリウム系複合酸化物焼結体及びその製造法

(57)【要約】

【構成】酸化セリウム50~99.9モル%を含むセリウム系複合酸化物において、1250~1600°Cで焼結した際の焼結体の相対密度が95%以上を示すセリウム系含有焼結性複合酸化物、1250~1600°Cで焼結したその焼結体、並びに金属酸化物換算濃度30~500g/リットルに調整した、各原料金属イオン含有溶液から複合塩沈殿物を得、この複合塩沈殿物を700~1200°Cで焼成した後、1250~1600°Cで焼結する前記焼結体の製造法。

【効果】前記複合酸化物は、低焼結性、加工性に優れ、固体電解質の電解質部材原料等として有用である。前記焼結体は、安価で加工が容易であり、焼結密度が高く、電解質とした場合、ガスの拡散が抑制され、電気的特性に優れる。前記製造法では、前記焼結体を、再現性良く、容易に得ることができる。

【特許請求の範囲】

【請求項1】 酸化セリウム50～99.9モル%を含み、更にセリウム以外の希土類金属酸化物の1種以上、酸化マグネシウム、酸化カルシウム、酸化ストロンチウム、酸化バリウム、酸化ジルコニウム、酸化ハフニウム、酸化ニオブ、酸化タンタル又はこれらの混合物0.1～50モル%を含むセリウム系複合酸化物において、1250～1600°Cで焼結した際の焼結体の相対密度が95%以上を示すことを特徴とするセリウム系含有焼結性複合酸化物。

【請求項2】 酸化セリウム50～99.9モル%を含み、更にセリウム以外の希土類金属酸化物の1種以上、酸化マグネシウム、酸化カルシウム、酸化ストロンチウム、酸化バリウム、酸化ジルコニウム、酸化ハフニウム、酸化ニオブ、酸化タンタル又はこれらの混合物0.1～50モル%を含むセリウム系複合酸化物を1250～1600°Cで焼結した、相対密度95%以上であるセリウム系複合酸化物焼結体。

【請求項3】 セリウムイオンをモル比で50～99.9モル%と、セリウム以外の希土類金属イオンの1種以上、マグネシウムイオン、カルシウムイオン、ストロンチウムイオン、バリウムイオン、ジルコニウムイオン、ハフニウムイオン、ニオブイオン、タンタルイオン又はこれらの混合物0.1～50モル%とを含む溶液を調製し、該溶液の濃度を含有される金属酸化物換算で30～500g/リットルに調整した後、アンモニア水溶液、炭酸アンモニウム水溶液、炭酸水素アンモニウム水溶液、シュウ酸水溶液又はこれらの混合物と混合して複合塩沈殿物を得、得られた複合塩沈殿物を700～1200°Cで焼成した後、1250～1600°Cで焼結することを特徴とする請求項2記載のセリウム系複合酸化物焼結体の製造法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、低温での焼結性に優れ、固体電解質型燃料電池(SOFC)、高温水蒸気電解装置等の電解質部材の原料として利用可能なセリウム系焼結性複合酸化物、該酸化物を焼結した焼結体及びその製造法に関する。

【0002】

【従来の技術】従来、セリウム系複合酸化物は、粉末の酸化セリウムを主成分とし、粉末化した他の成分の酸化物、炭酸塩、水酸化物等の塩を粉碎し、混合した後焼成する方法等により作製されている。このような複合酸化物は、SOFC、高温水蒸気電解装置等の電解質部材の原料等に使用されており、焼結後の高密度化、並びに加工時のガス拡散をなるべく抑制できる物性等を備えていることが望まれている。

【0003】しかしながら、従来の製造法により製造されたセリウム系複合酸化物は、低温での焼結性が悪く、

1650°C以上での焼結を行わなければ95%以上の相対密度が得られないのが実状である。このような高温での焼結を行った場合、得られる焼結体は、加工性が悪く、加工時のガス拡散を抑制することが困難であり、更にはコスト的にも高くなるという問題がある。

【0004】更に従来のセリウム系複合酸化物を焼結して、成形体を製造する場合には、成形助剤としての水等を必ず加える必要があり、製造工程が煩雑化すると共に、これらの添加物の添加により、得られる焼結体の物性低下等が生じる場合がある。

【0005】

【発明が解決しようとする課題】従って本発明の目的は、低温において優れた焼結性を有し、加工性、成形性に優れたセリウム系焼結性複合酸化物を提供することにある。本発明の他の目的は、加工性が容易であり、加工時のガス拡散が抑制でき、しかも安価であるセリウム系複合酸化物焼結体を提供することにある。本発明の別の目的は、前記焼結体を、再現性良く、容易に、しかも安価に調製することが可能であり、工業的な方法としても有効なセリウム系複合酸化物焼結体の製造法を提供することにある。

【0006】

【課題を解決するための手段】本発明によれば、酸化セリウム50～99.9モル%を含み、更にセリウム以外の希土類金属酸化物の1種以上、酸化マグネシウム、酸化カルシウム、酸化ストロンチウム、酸化バリウム、酸化ジルコニウム、酸化ハフニウム、酸化ニオブ、酸化タンタル又はこれらの混合物0.1～50モル%を含むセリウム系複合酸化物において、1250～1600°Cで焼結した際の焼結体の相対密度が95%以上を示すことを特徴とするセリウム系含有焼結性複合酸化物(以下複合酸化物Aと称す)が提供される。また本発明によれば、前記複合酸化物Aを1250～1600°Cで焼結した、相対密度95%以上であるセリウム系複合酸化物焼結体が提供される。更に本発明によれば、セリウムイオンをモル比で50～99.9モル%と、セリウム以外の希土類金属イオンの1種以上、マグネシウムイオン、カルシウムイオン、ストロンチウムイオン、バリウムイオン、ジルコニウムイオン、ハフニウムイオン、ニオブイオン、タンタルイオン又はこれらの混合物0.1～50モル%とを含む溶液を調製し、該溶液の濃度を含有される金属酸化物換算で30～500g/リットルに調整した後、アンモニア水溶液、炭酸アンモニウム水溶液、炭酸水素アンモニウム水溶液、シュウ酸水溶液又はこれらの混合物と混合して複合塩沈殿物を得、得られた複合塩沈殿物を700～1200°Cで焼成した後、1250～1600°Cで焼結することを特徴とする前記セリウム系複合酸化物焼結体の製造法が提供される。

【0007】以下本発明を更に詳細に説明する。本発明の複合酸化物Aは、酸化セリウムを主成分とし、後述す

る特定の金属酸化物を含み、1250~1600°Cで焼結した際の焼結体の相対密度が95%以上を示す。この際焼結体の相対密度とは、相対密度(%) = (見掛け密度/理論密度) × 100で算出した値である。ここで理論密度とは、測定する焼結前の複合酸化物の格子定数を、塩化ナトリウムを内部標準として(200)面の回折を基準にして、試料(複合酸化物の焼結体)の回折角を補正して求め、その値から算出した値である。また見掛け密度は、試料の質量と体積とから求めた値である。

【0008】本発明の複合酸化物Aは、酸化セリウム50~99.9モル%を含む。酸化セリウムの含有量が50モル%未満の場合には、焼結性が悪く、1250°C以上で焼結した場合、焼結体の相対密度が95%以上にならない。

【0009】本発明の複合酸化物Aは、前記酸化セリウムの他に、セリウム以外の希土類金属酸化物の1種以上、酸化マグネシウム、酸化カルシウム、酸化ストロンチウム、酸化バリウム、酸化ジルコニウム、酸化ハフニウム、酸化ニオブ、酸化タンタル又はこれらの混合物を0.1~50モル%含む。前記希土類金属酸化物としては、酸化イットリウム、酸化ランタン、酸化ラセオジム、酸化ネオジム、酸化サマリウム、酸化ガドリニウム等を挙げることができる。これらの成分は、公知のセリウム系複合酸化物の有効成分として知られた成分である。またこれらの金属酸化物の他に、前述の焼結後の相対密度が95%以上を示すものであれば、例えば製造時の原料等に起因する不可避的に混入される成分等が含まれていても良い。

【0010】本発明の複合酸化物Aの形状は、粒状又は粉状が好ましく、平均粒径0.1~3μm、比表面積5~20m²/g、タップ密度1.0~1.6g/cm³の範囲であるのが望ましい。

【0011】前記複合酸化物Aの製造法は、まずセリウムイオンをモル比で50~99.9モル%と、セリウム以外の希土類金属イオンの1種以上、マグネシウムイオン、カルシウムイオン、ストロンチウムイオン、バリウムイオン、ジルコニウムイオン、ハフニウムイオン、ニオブイオン、タンタルイオン又はこれらの混合物0.1~50モル%とを含む溶液を調製する。前記セリウム以外の希土類金属イオンとしては、イットリウムイオン、ランタンイオン、ラセオジムイオン、ネオジムイオン、サマリウムイオン、ガドリニウムイオン等を挙げることができる。これらのイオンを含む溶液を調製するには、各イオンを硝酸水溶液等として混合する方法等により得ることができる。

【0012】次に得られた溶液の濃度を、含有される金属酸化物換算で30~500g/リットル、好ましくは300~500g/リットルに調整する。この溶液の濃度が金属酸化物換算で500g/リットルを超える場合には、晶出が生じ、均一溶液とならず、また30g/リ

ットル未満の場合には沈澱物の結晶が成長し、次工程の反応に悪影響を与える。

【0013】次いで濃度調整した溶液を、アンモニア水溶液、炭酸アンモニウム水溶液、炭酸水素アンモニウム水溶液、シュウ酸水溶液又はこれらの混合物と混合して複合塩沈澱物を得る。この際、濃度調整した溶液に混合するこれら溶液の濃度は、アンモニア水溶液の場合、好ましくは1~2N、特に好ましくは1~1.5N、炭酸アンモニウム水溶液又は炭酸水素アンモニウム水溶液の場合、好ましくは50~200g/リットル、特に好ましくは100~150g/リットル、シュウ酸水溶液の場合、50~100g/リットル、特に好ましくは50~60g/リットルの範囲である。また前記濃度調整された溶液と、アンモニア水溶液、炭酸アンモニウム水溶液、炭酸水素アンモニウム水溶液、シュウ酸水溶液又はこれらの混合物との混合割合は、重量比で1:1~1:10が好ましい。この際得られる複合塩沈澱物としては、例えば複合水酸化物、複合炭酸塩等を挙げができる。

【0014】次に得られた複合塩沈澱物を、好ましくは乾燥後、700~1200°C、好ましくは750~1000°Cにおいて、1~10時間焼成することにより所望の低温焼結性は優れる複合酸化物Aを得ることができる。この際焼結温度が700~1200°Cの範囲外では、前記所望の相対密度を示す複合酸化物Aを得ることはできない。

【0015】本発明のセリウム系複合酸化物焼結体は、前記複合酸化物Aを焼結温度1250~1600°Cで焼結した、相対密度95%以上の焼結体である。

【0016】本発明の前記焼結体の製造法では、前述の複合酸化物Aを調製した後、焼結温度1250~1600°Cで、好ましくは1~20時間焼結する。好ましくは、得られた複合酸化物Aを、自動乳鉢等により、好ましくは平均粒径0.1~3μm程度に粉碎し、公知の成形器等を用いて所望の形状に成形した後、電気炉等を用いて焼結する方法等より行うことができる。この際成形工においては、従来のセリウム系複合酸化物のように、水等の成形助剤を使用せずに容易に成形することができる。また成形前の粉碎加工も従来のものより容易に行うことができる。

【0017】

【発明の効果】本発明の複合酸化物Aは、1250~1600°Cで焼結した場合、95%以上の相対密度を示すので、低温焼結性、加工性に優れ、固体電解質の電解質部材原料等として有用である。また本発明の焼結体は、前記複合酸化物Aを原料とするので、従来のセリウム系複合酸化物の焼結体に比較して加工が容易であり、焼結密度が高いので電解質として用いた場合、ガスの拡散が抑制され、電気的特性に優れており、しかも安価である。更に本発明の製造法では、このような焼結体を、再

現性良く、しかも安価で容易に得ることができ、工業的にも有効な方法である。

【0018】

【実施例】以下実施例及び比較例により本発明を更に詳細に説明するが、本発明はこれらに限定されるものではない。

【0019】

【実施例1】硝酸セリウム水溶液（三徳金属工業株式会社製：酸化セリウムとして500g/リットル含有）と、硝酸サマリウム水溶液（三徳金属工業株式会社製：酸化サマリウムとして250g/リットル含有）とを、酸化物換算で、 $CeO_2 : SmO_{1.5} = 80 : 20$ （モル比）となるように混合し、総重量500gの溶液を調製した。ここで $SmO_{1.5}$ は下記式化1と同意である。

【0020】

【化1】



【0021】次いで得られた溶液に、別に調製した160g/リットル炭酸アンモニウム水溶液3リットルを混合、反応させて、複合塩沈澱物を得た。得られた沈澱物は熱性させず、速やかに沪過し、150°Cで20時間乾燥させた後、900°Cで3時間焼成した。得られた焼成物を自動乳鉢で粉碎して平均粒径1.37μmの複合酸化物を得た。この粉碎には15分間を要した。

【0022】得られた複合酸化物2.5gを、直方体錠剤成形器（東洋油圧機械社製：2.5cm×0.5cm）と、加圧機（島津製作所社製）を用いて成形した。次いでアルミナボード（日本化学陶業社製、商品名「SA-Aアルミナ」純度99.5%）に同一組成の複合酸化物を敷砂として敷きつめ、その上に前記成形した複合酸化物を載置し、電気炉を用いて昇温速度10°C/分の条件で、表1に示す焼結温度まで昇温し、大気中で10時間、その温度で焼結した。その後降温速度10°C/分の条件で室温まで冷却して焼結体を得た。得られた焼結体は、各面が平行になるように耐水研磨紙（80番、180番、320番、600番、1000番、1500番）を用いて順次研磨した。次に研磨後の焼結体をノギスを用いて外径を計測すると共に、重量を電子天秤（精度：0.1mg）で秤量し、見掛け密度を測定した。各温度における焼結体の見掛け密度と相対密度とを表1に示す。尚、理論密度は得られた焼結体を粉碎し、粉末X線回折パターンを求めて、格子定数より計算した。

【0023】

【実施例2】硝酸セリウム水溶液（三徳金属工業株式会社製：酸化セリウムとして500g/リットル含有）と、硝酸サマリウム水溶液（三徳金属工業株式会社製：酸化サマリウムとして250g/リットル含有）と、更に硝酸カルシウム溶液（炭酸カルシウム（和光純薬工業社製）を硝酸に溶解し、濃度を酸化カルシウムとして400g/リットルに調整）とを、酸化物換算で、 $CeO_2 : SmO_{1.5} : CaO = 85 : 10 : 5$ （モル比）となるように混合し、総重量500gの溶液を調製した。以下実施例1と同様に複合酸化物を得、焼結温度を1500°Cとした以外は実施例1と同様に焼結体を調製し、見掛け密度、理論密度、相対密度を測定した。結果を表1に示す。

【0024】

$CeO_2 : SmO_{1.5} : CaO = 85 : 10 : 5$ （モル比）となるように混合し、総重量500gの溶液を調製した。以下実施例1と同様に複合酸化物を得、焼結温度を1500°Cとした以外は実施例1と同様に焼結体を調製し、見掛け密度、理論密度、相対密度を測定した。結果を表1に示す。

【0025】

【実施例3】硝酸セリウム水溶液（三徳金属工業株式会社製：酸化セリウムとして500g/リットル含有）と、硝酸サマリウム水溶液（三徳金属工業株式会社製：酸化サマリウムとして250g/リットル含有）と、更に硝酸ストロンチウム溶液（硝酸ストロンチウム（和光純薬工業社製）を水に溶解し、濃度を酸化ストロンチウムとして400g/リットルに調整）とを、酸化物換算で、 $CeO_2 : SmO_{1.5} : SrO = 85 : 10 : 5$ （モル比）となるように混合し、総重量500gの溶液を調製した。以下実施例1と同様に複合酸化物を得、焼結温度を1500°Cとした以外は実施例1と同様に焼結体を調製し、見掛け密度、理論密度、相対密度を測定した。結果を表1に示す。

【0026】

【比較例1】粉状の酸化セリウム及び酸化サマリウムを、 $CeO_2 : SmO_{1.5} = 80 : 20$ （モル比）の配合割合で、総重量が50gとなるように、それぞれ電子天秤で秤量し、自動乳鉢（日陶科学社製）で30分間粉碎混合した。次いでアルミナるつぼに移し、電気炉を用いて昇温速度10°C/分で1350°Cまで昇温し、大気中で10時間保持した後、降温速度10°C/分で室温まで冷却した。次いで自動乳鉢で実施例1と同様に粉碎して平均粒径1.79μmの複合酸化物を得た。この粉碎には実施例1の2倍の時間（30分）を要した。得られた複合酸化物1.9gに、成形助剤として水約20mlを加え、メノウ乳鉢で15分間混合した。

【0027】これを直方体錠剤成形器（東洋油圧機械社製：2.5cm×0.5cm）と、加圧機（島津製作所社製）を用いて成形した。次いでアルミナボード（日本

化学陶業社製、商品名「SSA-Aアルミナ」純度99.5%）に同一組成の複合酸化物を歎砂として歎きつめ、その上に前記成形した複合酸化物を載置し、電気炉を用いて昇温速度10°C/分の条件で、表1に示す焼結温度まで昇温し、大気中で10時間その温度で焼結した。その後降温速度10°C/分の条件で室温まで冷却して焼結体を得た。尚、成形助剤を入れない場合には焼結性が上がらなかった。得られた焼結体は、実施例1と同様に処理した後、見掛け密度、理論密度、相対密度を測定した。結果を表1に示す。

【0028】

【比較例2】粒状の酸化セリウム、酸化サマリウム及び炭酸カルシウムをCeO₂: SmO_{1.5}: CaO=85:10:5(モル比)の配合割合で、総重量が50gとなるように、それぞれ電子天秤で秤量した後、比較例1と同様に複合酸化物を調製した。得られた複合酸化物を1650°Cで焼結した以外は、比較例1と同様に処理し、見掛け密度、理論密度、相対密度を測定した。結果を表1に示す。

【0029】

* 【比較例3】粒状の酸化セリウム、酸化サマリウム及び炭酸ストロンチウムを、CeO₂: SmO_{1.5}: SrO=85:10:5(モル比)の配合割合で、総重量が50gとなるように、それぞれ電子天秤で秤量した後、比較例1と同様に複合酸化物を調製した。得られた複合酸化物を1600°Cで焼結した以外は、比較例1と同様に処理し、見掛け密度、理論密度、相対密度を測定した。結果を表1に示す。

【0030】

10 【比較例4】粒状の酸化セリウム、酸化サマリウム及び炭酸バリウムをCeO₂: SmO_{1.5}: BaO=85:10:5(モル比)の配合割合で、総重量が50gとなるように、それぞれ電子天秤で秤量した後、比較例1と同様に複合酸化物を調製した。得られた複合酸化物を1600°Cで焼結した以外は、比較例1と同様に処理し、見掛け密度、理論密度、相対密度を測定した。結果を表1に示す。

【0031】

【表1】

*20

	CeO ₂ (モル)	SmO _{1.5} (モル)	MO (モル)	複合密度 (g/cm ³)	焼結温度 (°C)	見掛け密度 (g/cm ³)	相対密度 (%)
実施例1	0.80	0.20	-	7.133	1650 1450 1250 1150 1050	6.952 6.035 6.973 6.395 6.256	97.5 98.6 97.8 89.7 73.7
実施例2	0.85	0.10	0.05 (CaO)	6.961	1600	6.827	96.2
実施例3	0.85	0.10	0.05 (SrO)	6.982	1600	6.793	97.3
実施例4	0.85	0.10	0.05 (BaO)	7.132	1600	6.875	96.4
比較例1	0.80	0.20	-	7.133	1650 1500 1450 1350	6.721 6.211 6.047 5.184	94.2 87.1 84.8 72.4
比較例2	0.85	0.10	0.05 (CaO)	6.961	1650	6.924	85.1
比較例3	0.85	0.10	0.05 (SrO)	6.982	1600	6.988	87.2
比較例4	0.85	0.10	0.05 (BaO)	7.132	1600	6.012	84.3

【手続補正書】

【提出日】平成6年12月21日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】0002

【補正方法】変更

【補正内容】

【0002】

【従来の技術】従来、セリウム系複合酸化物は、粉末の酸化セリウムを主成分とし、粉末化した他の成分の酸化物、炭酸塩、水酸化物等の塩を粉碎し、混合した後焼成

する方法等により作製されている。このような複合酸化物は、SOFC、高温水蒸気電解装置等の電解質部材の原料等に使用されており、焼結後の高密度化、並びにガス拡散をなるべく抑制できる物性等を備えていることが望まれている。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0003

【補正方法】変更

【補正内容】

【0003】しかしながら、従来の製造法により製造されたセリウム系複合酸化物は、低温での焼結性が悪く、 1650°C 以上での焼結を行わなければ95%以上の相対密度が得られないのが実状である。このような高温での焼結を行った場合、得られる焼結体は、加工性が悪く、ガス拡散を抑制することが困難であり、更にはコスト的にも高くなるという問題がある。

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0005

【補正方法】変更

【補正内容】

【0005】

【発明が解決しようとする課題】従って本発明の目的は、低温において優れた焼結性を有し、加工性、成形性に優れたセリウム系焼結性複合酸化物を提供することにある。本発明の他の目的は、加工が容易であり、ガス拡散が抑制でき、しかも安価であるセリウム系複合酸化物焼結体を提供することにある。本発明の別の目的は、前記焼結体を、再現性良く、容易に、しかも安価に調製することが可能であり、工業的な方法としても有効なセリ

ウム系複合酸化物焼結体の製造法を提供することにある。

【手続補正4】

【補正対象書類名】明細書

【補正対象項目名】0026

【補正方法】変更

【補正内容】

【0026】

【比較例1】粉状の酸化セリウム及び酸化サマリウムを、 $\text{CeO}_2 : \text{SmO}_{1.5} = 80 : 20$ (モル比) の配合割合で、總重量が50gとなるように、それぞれ電子天秤で秤量し、自動乳鉢(日陶科学社製)で30分間粉碎混合した。洗いてアルミナるつぼに移し、電気炉を用いて昇温速度 $10^{\circ}\text{C}/\text{分}$ で 1350°C まで昇温し、大気中で10時間仮焼した後、降温速度 $10^{\circ}\text{C}/\text{分}$ で室温まで冷却した。次いで自動乳鉢で実施例1と同様に粉碎して平均粒径 $1.79 \mu\text{m}$ の複合酸化物を得た。この粉碎には実施例1の2倍の時間(30分)を要した。得られた複合酸化物1.9gに、成形助剤として水約20mlを加え、メノウ乳鉢で15分間混合した。

page 8

OLYTR

double oxide sinter - obtnd. by
of e.g. magnesium, strontium or
q. soln. of ammonia to pptns.,
ng and sintering prod.

116
KU KINZOKU KOGYO KK

96.07.02 (9636) 69

P-311722
P-311722
C04B-035/00 C25B-009/00
HO1M-008/12

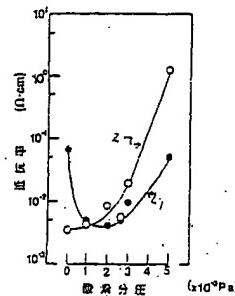
-A) contg. double oxide contains
.4 and 0.1-50 mol.% oxide of Mg,
Tr, Hf, Nb, Ta, or their mixt. It
sinter having at least 95%
nsity when sintered at
deg.C. The sinter given by sintering
ium contg. double oxide is also
cdn. of the sinter is also
ere a source soln. which contains
1.4 cerium ions and 0.1-50 mol.%
earth metal ions selected from Mg,
Tr, Hf, Nb, or Ta is prod.; the
concen. is controlled within
.. It is mixed with the q. soln. of
cer, ammonium carbonate, ammonium
carbonate, oxalic acid, or their
obtain precipitates which are fired
00 deg.C., and sintered at
deg. C.
a source material for the
te of solid oxide fuel cells or high
am electrolysis plants.
- A sinter with at least 95%
density can be obtnd. at lower temp.
it is low cost and easy to process.
ng gas permeation when it is used as
electrolyte of fuel cells. (Dwg. 0/0)

1/36
51
it exhaust gas from car or power plant
ming cathode contg. catalyst layer on
ce of solid electrolyte with anode on
face
J01 J04
... as rnm SCI & TECHNOLOGY

Page 7

SOLID ELECTROLYTE

-3- (WPIL)



ACCESSION NUMBER 96-360139/36
SECONDARY ACCESSION C96-113500
XRPX N96-303679
TITLE Transparent conductive film mfr. - by forming
film of zinc sulphate(s) on substrate by
sputtering, using target alloy of zinc and
tin and oxide, under mixed gas atmos.
L02 L03 X12
(GNBZ) GUNSE KK
1
1
JPOB171824-A 96.07.02 (9636) 5p
HO1B-013/00
94.03.27 94JP-079645
94.03.27 94JP-079645-
C01G-019/02 C23C-014/08 C23C-014/34
C23C-016/40 HO1B-005/14 HO1B-013/00
(JPOB171824-A)
The transparent conductive film of Zn₂SnO₄ or
ZnSnO₃ is formed on a substrate by
sputtering, using target of alloy of Zn and
Sn and its oxide, under atmos. of mixed inert
gas and oxidizing gas.
ADVANTAGE - Provides a transparent conductive
film, having good chemical stability for
temp, acid, and alkali, having low resistance
and transmissivity, and can dissolve faults
of Zn group transparent conductive film.
(Dwg.1/2)
WPG7PVV1.GIF

DERVENT CLASSES
PATENT ASSIGNEE
NUMBER OF PATENTS 1
NUMBER OF COUNTRIES 1
PATENT FAMILY JPOB171824-A
PRIORITY 94.03.27 94JP-079645
APPLICATION DETAILS 94.03.27 94JP-079645-
INT'L. PATENT CLASS. C01G-019/02 C23C-014/08 C23C-014/34
C23C-016/40 HO1B-005/14 HO1B-013/00
(JPOB171824-A)
ABSTRACT
IMAGE FILENAME WPG7PVV1.GIF

-4- (WPIL)
ACCESSION NUMBER 96-358378/36
SECONDARY ACCESSION C96-112924
XRPX N96-302214

SOLID ELECTROLYTE

TITLE

Cerium-contg. double oxide sinter - obtd. by mixing oxide of e.g. magnesium, strontium or barium with aq. soln. of ammonia to ppt., and then firing and sintering prod.

E37 J03 L03 X16

(SANT-) SANTOKU KINZOKU KOGYO KK

1

1

JP08169713-A 96.07.02 (9636) 6p

C01F-017/00

94.12.15 94JP-311722

94.12.15 94JP-311722

C01F-017/00 C04B-035/50 C25B-009/00

H01M-008/02 H01M-008/12

(JP08169713-A)

New cerium-contg. double oxide contains 50-99.9 mol.% and 0.1-50 mol.% oxide of Mg, Ca, Sr, Ba, Zr, Hf, Nb, Ta, or their mixt. It provides a sinter having at least 95% relative density when sintered at 1250-1600deg.C. The sinter given by sintering the new cerium contg. double oxide is also claimed. Prodn. of the sinter is also claimed, where a source soln. which contains 50-99.9 mol.% cerium ions and 0.1-50 mol.% other rare earth metal ions selected from Mg, Ca, Sr, Ba, Zr, Hf, Nb, or Ta is prep'd.; the metal oxide concn. is controlled within 30-500 g/l. It is mixed with the aq. soln. of ammonia water, ammonium carbonate, ammonium hydrogen carbonate, oxalic acid, or their mixt. to obtain precipitates which are fired at 700-1200 deg.C., and sintered at 1250-1600deg. C.

USE - As a source material for the electrolyte of solid oxide fuel cells or high temp. steam electrolysis plants.

ADVANTAGE - A sinter with at least 95% relative density can be obtd. at lower temp. The sinter is low cost and easy to process, preventing gas permeation when it is used as an electrolyte of fuel cells. (Dwg.0/0)

Robin →
ordered
Being
translated

-5- (WPIL)

ACCESSION NUMBER

96-357473/36

SECONDARY ACCESSION

C96-112651

TITLE

Treatment exhaust gas from car or power plant - by forming cathode contg. catalyst layer on first face of solid electrolyte with anode on second face

E36 H06 J01 J04

(AGEN) AGENCY OF IND SCI & TECHNOLOGY

1

1

JP08168673-A 96.07.02 (9636) 9p

B01J-023/22

DERWENT CLASSES

PATENT ASSIGNEE

NUMBER OF PATENTS

NUMBER OF COUNTRIES

PATENT FAMILY